ENTROPY BALANCE IN PHOTOSYNTHESIS

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Although photosynthesis is usually approached from the energy point of view, it is more likely that the entropy aspects of this process will intrigue the physical scientist, and especially for the following reason. As was emphasized, notably by Schrödinger,[1] energy alone is incapable of sustaining the life of a plant or any other organism: moreover, there must be a continuous influx of enough negative entropy to at least balance the increase of entropy that inevitably accompanies the irreversible processes occurring inside the organism; otherwise, it would rapidly decay into the lifeless state of maximum entropy.[2] Green plants acquire this negative entropy, along with energy, in the course of photosynthesis from the sunlight incident on their leaves.

To the physicist it must appear rather important to investigate quantitatively whether or not the Second Law of Thermodynamics is obeyed in photosynthesis, where both radiation and living matter are involved. This very problem was tackled by Brittin and Gamow[3] in an earlier paper, but as their treatment, in our opinion, suffers from some theoretical oversights (notably the application of thermostatic formulas to nonequilibrium radiation), we deem it essential to study the problem anew with the aim of improving on the conclusions of these authors.

In its over-all effect, the process of photosynthesis, taking place in a leaf exposed to monochromatic solar radiation of frequency ν, can be represented by the photochemical reaction

$$6CO_2 + 6H_2O + nh\nu \rightarrow C_6H_{12}O_6 + 6O_2, \tag{1}$$
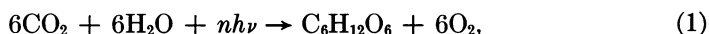
where $h\nu$ is the energy of an incident photon and n denotes the number of photons participating in the synthesis of one molecule of glucose. To render possible the computation of all the entropy changes associated with this reaction, we have to approximate the actual processes and the system in which they occur, by the following model.

The Sun, acting as a black body, emits unpolarized light of frequency ν, which traverses empty space before impinging on a plant leaf (we ignore dissipation due to interplanetary dust and the Earth's atmosphere) held at constant temperature T_E and pressure p, taken to be room temperature and atmospheric pressure, respectively. When radiation of volume V and energy U_ν is absorbed by the leaf, only the fraction η of the energy is utilized in the reaction (1), and thus reappears as the excess of the free energy of the products over that of the chemical reactants; the remaining fraction $1 - \eta$, we assume, is emitted by the leaf as equilibrium radiation of temperature T_E and volume V. The accompanying (negative) increase of the entropy of the reacting molecules and the (positive) increase of the radiation entropy are ΔS_m and ΔS, say. No entropy changes other than those enumerated are supposed to occur. Then we can assert that, lest the Second Law be violated, the increased ΔS of the radiation entropy cannot

be less than the decrease $-\Delta S_m$ of the molecular entropy. ΔS_m is known empirically; we now set out to determine ΔS.

First, let us recall that for a system of equilibrium (i.e., blackbody) radiation a simple set of properties obtains, due to such a system's being spatially homogeneous and isotropic. Notably, the radiation is characterized by:[2] a definite temperature T (the same for all frequencies), energy volume density $u^0 = aT^4$, entropy volume density $s^0 = (4/3)aT^3$, and a distribution of the energy u^0 over the spectrum in accordance with Planck's law

$$u_\nu^0(T) = (8\pi h\nu^3/c^3)(e^{h\nu/kT} - 1)^{-1}. \tag{2}$$

It must be realized, however, that the (anisotropic) radiation given off by the Sun is a nonequilibrium system and therefore not covered by these simple formulas. A more sophisticated description is required,[4] based on the flux parameters K_ν (the specific radiation intensity of frequency ν) and L_ν (the specific intensity of entropy radiation). K_ν is defined in such a fashion that $K_\nu \, d\nu \, dt \, d\sigma \cos \Theta \, d\Omega$ furnishes the radiation energy, in the frequency interval $d\nu$, that passes in time dt through an element of area $d\sigma$, and inside an element of solid angle $d\Omega = \sin \Theta \, d\Theta \, d\varphi$, in a direction forming an angle Θ with the normal to the area. L_ν has a corresponding definition, with "entropy" replacing "energy." Thus, K_ν as well as L_ν, are functions of both position $\mathbf{r}$ and the polar angles of the direction under consideration. The densities of energy and entropy are derivable from the specific intensities in this manner:[5]

$$u_\nu(\mathbf{r}) = (1/c) \int K_\nu \, d\Omega \quad \text{and} \quad s_\nu(\mathbf{r}) = (1/c) \int L_\nu \, d\Omega. \tag{3}$$

For blackbody radiation, the integrations in (4) can be carried out immediately to give

$$u_\nu^0 = (4\pi/c)K_\nu^0 \quad \text{and} \quad s_\nu^0 = (4\pi/c)L_\nu^0. \tag{4}$$

The first of these equations leads, with the aid of equation (2), to

$$K_\nu^0 = (2h\nu^3/c^2)(e^{h\nu/kT} - 1)^{-1}. \tag{5}$$

L_ν^0, on the other hand, is obtainable from the equation[6]

$$L_\nu^0 = (2k\nu^2/c^2)[(1 + \xi) \log (1 + \xi) - \xi \log \xi], \tag{6}$$

wherein

$$\xi = c^2 K_\nu^0/2h\nu^3 = (e^{h\nu/kT} - 1)^{-1}. \tag{7}$$

To discover $u_\nu(\mathbf{r})$ and $s_\nu(\mathbf{r})$ at any point in the (anisotropic) radiation field of the Sun, we start from the theoretical observation that in empty space both intensities K_ν and L_ν will remain constant along the path of a light ray. Thus, at the surface of the Earth, radiation arrives from the Sun with the same intensities it had on leaving the surface of the Sun. We suppose next that the radiation emerges from the Sun with intensities that are independent of direction and furnished by the blackbody formulas (5) and (6) with $T = T^*$, the effective

temperature of the Sun. Under these assumptions, equation (3) asserts that the energy density, for example, at the surface of the Earth will be

$$u_\nu(r) = (1/c)\int_\Omega K_\nu^0(T^*)d\Omega' = (\Omega/c)K_\nu^0(T^*) = (\Omega/4\pi)u_\nu^0(T^*), \qquad (8)$$

where r is the distance from the center of the Sun to the surface of the Earth and Ω the solid angle subtended by the Sun at the Earth. If R denotes the radius of the Sun, a simple geometric argument will show that

$$\Omega = 2\pi\{1 - [1 - (R/r)^2]^{1/2}\} \approx \pi(R/r)^2,$$

and consequently,

$$u_\nu(r) = (R/2r)^2 u_\nu^0(T^*). \qquad (9)$$

The *dilution factor* $(R/2r)^2$, measuring here the deviation of the energy density from its value for equilibrium, obtains likewise for the entropy density. Hence, at the surface of the Earth,

$$s_\nu(r) = (R/2r)^2 s_\nu^0(T^*). \qquad (10)$$

We are now able to write down the entropy S_ν of the monochromatic radiation absorbed by a leaf, in terms of its energy U_ν. From equations (4), (9), and (10),

$$S_\nu/U_\nu = s_\nu(T^*)/u_\nu(T^*) = L_\nu^0(T^*)/K_\nu^0(T^*),$$

so that

$$S_t = (kU_\nu/h\nu)[(1 + 1/\xi^*) \log (1 + \xi^*) - \log \xi^*], \qquad \xi^* = \xi(T^*). \quad (11)$$

By hypothesis, only the part ηU_ν of the energy is used in the photochemical reaction (1), while the remainder $(1 - \eta)U_\nu$ is emitted as blackbody radiation having volume V, temperature $T_E \equiv T$, and thus the entropy $(4/3)(1 - \eta)U_\nu/T$. Subtraction of the entropy S_ν reveals that the increase of radiation entropy, when one molecule of glucose is formed $(\eta U_\nu = nh\nu)$, is

$$\Delta S = \frac{4}{3}\frac{1}{T}\frac{1 - \eta}{\eta}\, nh\nu +$$
$$\frac{nk}{\eta}\left[e^{h\nu/kT^*} \log (1 - e^{-h\nu/kT^*}) - \log (e^{h\nu/kT^*} - 1)\right]. \quad (12)$$

If we take the effective temperature of the Sun to be $T^* = 5{,}700°$K, so that $h/kT^* = 8.43 \times 10^{-15}$ sec, then $h\nu/kT^*$ exceeds 3.6 for all wavelengths smaller than 7,000 Å. In other words, throughout the whole visible spectrum, at least, $\exp h\nu/kT^* \gg 1$, and one can, without significant error, approximate equation (12) by

$$\frac{\eta\Delta S}{nh\nu} = \frac{4}{3}\frac{1 - \eta}{T} - \frac{k}{h\nu} - \frac{1}{T^*}. \qquad (13)$$

It may be noted that the frequency-dependent term appearing on the right is negligible only if $h\nu \gg kT^*$; that is, in the ultraviolet region of the spectrum and beyond.

Finally, we insert $T = 300°$K and $T^* = 5,700°$K in (13) and apply the formula to light of wavelength 7,000 Å (red end of spectrum), i.e., $\nu = 4.28 \times 10^{14}$ sec^{-1}. If the calorie is used as energy unit, the result is $\Delta S/n = 172/\eta - 182$, or if we put $n = 3$ (as Brittin and Gamow do[3]), $\Delta S = 516/\eta - 546$.   This must now be compared with the decrease of molecular entropy accompanying the formation of 1 mole of glucose,[7] $-\Delta S_m = 40$ cal mole^{-1}deg^{-1}.

We conclude that the Second Law will be valid, i.e., $\Delta S > -\Delta S_m$, provided $\eta < 0.88$.   Experimentally, the efficiency of photosynthesis in red light is 59 per cent,[8] so that the above requirement is certainly satisfied.

[1] Schrödinger, E., *What is Life?* (Cambridge University Press, 1944).

[2] Yourgrau, W., A. van der Merwe, and G. Raw, *Irreversible and Statistical Thermophysics* (New York: The Macmillan Co., 1966), pp. 50–53.

[3] Brittin, W., and G. Gamow, "Negative entropy and photosynthesis," these PROCEEDINGS, **47**, 724 (1961).

[4] Planck, M., *The Theory of Heat Radiation* (New York: Dover Publications, Inc., 1959). We presuppose unpolarized radiation and accordingly employ a K_ν twice as large as that of Planck.

[5] *Ibid.*, equation (23).

[6] *Ibid.*, equation (278).

[7] von Bertalanffy, L., *Theoretische Biologie* (Bern: A. Francke Verlag, 1951), p. 114.

[8] *Ibid.*, p. 40.